

CLAIMS

1. A process for producing a multimodal ethylene polymer, which process comprises the following steps:

1) contacting in a first gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about 70 °C to about 110 °C, a supported titanium magnesium catalyst precursor, cocatalyst, and a gaseous composition, the gaseous composition having;

i) a mole ratio of alpha-olefin to ethylene of from about 0.01:1 to about 0.8:1; and optionally

ii) a mole ratio of hydrogen to ethylene of from about 0.001:1 to about 0.3:1, to produce a high molecular weight polymer(HMW); and

2) transferring the HMW polymer from step 1 to a second gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about 70 °C to about 110 °C, with a gaseous composition having;

i) a mole ratio of alpha-olefin to ethylene less than that in Step 1 and of from about 0:0005:1 to about 0.01:1; and

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.01:1 to about 3:1 to form a polymer blend product; and

3) melting the polymer blend product in an extruder having a mixer vent wherein;

ii) the mixture vent has an oxygen concentration of from about 0.05 to about 6 volume percent oxygen in nitrogen; and

ii) the extrusion temperature is sufficient to melt the polymer and achieve tailoring in the presence of oxygen; and

4) passing the molten polymer blend through one or more active screens, wherein in the case of two or more active screens, the screens are positioned in series, each active screen having a micron retention size of from about 2 to about 70, at a mass flux of about 5 to about 100 lb/hr/in² (1.0 to 20 kg/s/m²) to form a screened molten polymer blend.

2. The process of Claim 1 wherein;

1) the gaseous composition in Step 1) has;

i) a mole ratio of alpha-olefin to ethylene of from about 0.02:1 to about 0.35:1;

and

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.01:1 to about 0.2:1, and

2) the gaseous composition in Step 2) has;

i) a mole ratio of alpha-olefin to ethylene of less than or equal to about 0.007:1; and optionally

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.5:1 to about 2.2:1;

3) in Step 3, the extrusion temperature is from about 220 to about 270 °C; and

wherein the ratio of the weight of polymer prepared in the first gas phase reactor used in Step 1) to the weight of polymer prepared in the second gas phase reactor used in Step 2) is in the range of about 30:70 to about 70:30.

3. The process of Claim 2 wherein the ratio of the weight of polymer prepared in the first gas phase reactor used in Step 1 to the weight of polymer prepared in the second gas phase reactor used in Step 2 is in the range of about 40:60 to about 60:40; the mole ratio of alpha olefin to ethylene in Step 1 is from about 0.02:1 to about 0.35:1 and in Step 2 is from about 0.001:1 to about 0.007:1; and in Step 3, the extrusion temperature is from about 230 to about 260 °C.

4. The process of any of Claims 1 through 3 wherein the polymer produced in Step 2 has a density of from 0.970 to 0.975 g/cm³.

5. A multimodal polyethylene composition having;

1) a density of at least about 0.940 g/cm³ as measured by ASTM Method D-1505;

2) a melt flow index (I₅) of from about 0.2 to about 1.5 g/10 min (as measured by ASTM D-1238, measured at 190 °C and 5 kilograms);

3) a melt flow index ratio (I₂₁/I₅) of from about 20 to about 50;

4) a molecular weight distribution, Mw/Mn, of from about 20 to about 40; and

5) a bubble stability measured on an HS50S stationary extrusion system with an BF 10-25 die, HK 300 air ring, A8 take off, and WS8 surface winder, all commercially available from Hosokawa Alpine Corporation, with a 100 mm die diameter having a 50 mm 21:1 L/D grooved feed extruder used according to the conditions described herein for a film of about 6 X 10⁻⁶ m thickness of at least about 1.22 m/s line speed, at least about 45 kg/hr (0.013 kg/sec) output rate, or at least about 0.5 lb/hr/rpm (0.0000011 kg/s/rps) specific output rate or a combination thereof.

6) a dart impact on 12.5 micron (1.25 X 10⁻⁵ m) film of at least 300 g; measured according to ASTM 1709, Method A;

the composition comprising;

A) a high molecular weight fraction which;

a) is present in an amount of from about 30 to about 70 weight percent (based on the total weight of the composition);

b) has a density of at least about 0.860 g/cm^3 as measured by ASTM D-1505;

c) has a melt flow index (I_{21}) of from about 0.01 to about 50 g/10 min (as measured by ASTM D-1238, measured at 190°C and 21.6 kilograms); and

d) a melt flow index ratio (I_{21}/I_5) of from about 6 to about 12; and

B) a low molecular weight fraction which;

a) is present in an amount of from about 30 to about 70 weight percent (based on the total weight of the composition);

b) has a density of at least about 0.900 g/cm^3 as measured by ASTM D-1505;

c) has a melt flow index (I_2) of from about 0.5 to about 3000 g/10 min (as measured by ASTM D-1238, measured at 190°C and 2.16 kilograms);

d) a melt flow index ratio (I_{21}/I_5) of from about 5 to about 15; and

e) is prepared using a mole ratio of alpha olefin to ethylene less than that in the high molecular weight fraction of less than or equal to about 0.01:1.

6. The multimodal polyethylene composition of Claim 5 wherein;

1) the density is from about 0.945 to about 0.955 g/cm^3 ;

2) the melt flow index (I_5) is of from about 0.25 to about 1.0 g/10 min;

3) the melt flow index ratio (I_{21}/I_5) is of from about 24 to about 40;

4) the molecular weight distribution, M_w/M_n is from about 22 to about 38; and

5) the bubble stability is greater than about 1.32 m/s line speed or from about 0.0000017 to 0.000027 kg/s/rps specific output rate or a combination thereof;

the composition comprising;

A) a high molecular weight fraction which;

a) is present in an amount of from about 40 to about 60 weight percent (based on the total weight of the composition);

b) has a density of from about 0.890 to about 0.940 g/cm^3 ;

c) has a melt flow index (I_{21}) of from about 0.2 to about 12 g/10 min; and

- d) a melt flow index ratio (I_{21}/I_5) of from about 7 to about 12; and
- B) a low molecular weight fraction which;
 - a) is present in an amount of from about 40 to about 60 weight percent (based on the total weight of the composition);
 - b) has a density of from about 0.910 to about 0.975 g/cm³;
 - c) has a melt flow index (I_2) of from about 1.0 to about 1,000 g/10 min;
 - d) a melt flow index ratio (I_{21}/I_5) of from about 6 to about 12; and
 - e) the ratio of alpha olefin to ethylene is less than that in the high molecular weight fraction and less than or equal to about 0.01:1.

7. The multimodal polyethylene composition of Claim 6 wherein;

1) the molecular weight measured by Gel Permeation Chromatography is from about 90,000 to about 420,000.

2) the bubble stability is reflected in an output rate of from about 0.013 to 0.13 kg/s; the composition comprising;

A) a high molecular weight fraction which;

a) has a melt flow index (I_{21}) of from about 0.2 to about 0.4 g/10 min; and

b) a molecular weight of from about 135,000 to about 445,000;

c) is prepared using a mole ratio of alpha olefin to ethylene of from about 0.02:1 to about 0.35:1 and

B) a low molecular weight fraction which;

a) has a density of from about 0.970 to about 0.975 g/cm³;

b) has a molecular weight of from about 15,800 to about 35,000; and

c) is prepared using a mole ratio of alpha olefin to ethylene of less than or equal to about 0.007:1.

8. The multimodal polyethylene composition of any of Claims 5 through 7 wherein the composition is tailored sufficiently to produce an increase of melt flow ratio (I_{21}/I_5) of from about 1 to about 4 units as compared with the same composition without tailoring.

9. The multimodal polyethylene composition of any of Claims 5 through 7 which;

i) when fabricated into a film of 0.5 mils (1.27×10^{-5} m) thickness, has a dart impact of greater than about 400 g;

ii) when fabricated into a film of 1.0 mils (2.54×10^{-5} m) thickness, has a film appearance rating of greater than or equal to 20; and

iii) when fabricated into a blown film has (a) a bubble stability of at least about 240 ft/min (1.22 m/s) line speed, (b) can be used to produce blown film of 6 micron (6×10^{-6} m) thickness at actual output rates of from about 50 to about 1100 lb/hr (0.0063 to 0.14 kg/s) or (c) specific output rates of from about 0.5 to about 15 lb/hr/rpm (1.05×10^{-6} to 3.15×10^{-5} kg/s/rps), or a combination of at least 2 of (a) (b) and (c).

10. The multimodal polyethylene composition of Claim 5 produced by a process comprising:

1) contacting in a first gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about 70 °C to about 110 °C, a supported titanium magnesium catalyst precursor, cocatalyst, and a gaseous composition, the gaseous composition having;

i) a mole ratio of alpha-olefin to ethylene of from about 0.01:1 to about 0.8:1; and optionally

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.001:1 to about 0.3:1,

to produce a high molecular weight polymer(HMW); and

2) transferring the HMW polymer from step 1 to a second gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about 70 °C to about 110 °C, with a gaseous composition having;

i) a mole ratio of alpha-olefin to ethylene of from about 0.0005:1 to about 0.01:1; and

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.01:1 to about 3:1

to form a polymer blend product; and

3) melting the polymer blend product in an extruder having a mixer vent wherein;

ii) the mixture vent has an oxygen concentration of from about 0.05 to about 6 volume percent oxygen in nitrogen; and

ii) the extrusion temperature is sufficient to melt the polymer and result in tailoring in the presence of the oxygen; and

4) passing the molten polymer blend through one or more active screens, wherein in the case of two or more active screens, the screens are positioned in series, each active screen having a micron retention size of from about 2 to about 70, at a mass flux of about 5 to about 100 lb/hr/in² (1.0 to 20 kg/s/m²) to form a screened molten polymer blend.

11. The multimodal polyethylene composition of Claim 10 wherein in the process;

1) the gaseous composition in step 1) has;

i) a mole ratio of alpha-olefin to ethylene of from about 0.02:1 to about 0.35:1;

and

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.01:1 to about 0.2:1, and

2) the gaseous composition in step 2) has;

i) a mole ratio of alpha-olefin to ethylene of from about 0.001:1 to about 0.007:1; and optionally

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.5:1 to about 2.2:1; and

wherein

3) the ratio of the weight of polymer prepared in the first gas phase reactor used in step 1) to the weight of polymer prepared in the second gas phase reactor used in step 2) is in the range of about 30:70 to about 70:30.

12. The multimodal polyethylene composition of Claim 10 or 11 which, when fabricated into a film using a HS50S stationary extrusion system with an BF 10-25 die, HK 300 air ring, A8 take off, and WS8 surface winder, all commercially available from Hosokawa Alpine Corporation, with a 100 mm die diameter having a 50 mm 21:1 L/D grooved feed extruder has a vertical bubble stability described by:

Alpine film line vertical bubble stability (in ft/min) = $275.05 - 0.000081 * M_z + 0.0000735 * M_{z+1} (BB) + 0.0001312 * \text{viscosity} (P) @ 0.1 \text{ sec}^{-1} \text{ shear rate} + 1.0033E-9 * (\text{viscosity} (P) @ 0.1 \text{ sec}^{-1} \text{ shear rate})^2 - 0.026764 * \text{viscosity} (P) @ 100 \text{ sec}^{-1} \text{ shear rate}$ [where (BB) is backbone, E is exponent of base 10] or

Alpine film line vertical bubble stability (in m/s) = $\{0.005\} \{275.05 - 0.000081 * M_z + 0.0000735 * M_{z+1} (BB) + (0.0001312 * 0.1 * \text{viscosity} (Pa \cdot s) @ 0.1 \text{ sec}^{-1} \text{ shear rate}) + 1.0033E-9 * [(0.1) (\text{viscosity} (Pa \cdot s) @ 0.1 \text{ sec}^{-1} \text{ shear rate})]^2 - (0.026764 * 0.1 * \text{viscosity} (Pa \cdot s) @ 100 \text{ sec}^{-1} \text{ shear rate})\}$

13. The multimodal polyethylene composition of Claim 10 or 11 wherein when made into a film has a Dart Drop calculatable using the equation: Dart drop (g) = $469.9 - 54.8 * (G'/G'' @ 0.01 \text{ shear rate}) - 91.4 (G'/G'' @ 0.01 \text{ shear rate})^2$.

14. A film comprising the multimodal polyethylene composition of Claim 10 or 11.

15. A multimodal modal polyethylene film which;

i) when fabricated into a film of 0.5 mils (1.27×10^{-5} m) thickness has a dart impact strength of greater than about 300 g,

ii) when fabricated into a film of 1.0 mils (2.54×10^{-5} m) thickness has a film appearance rating of greater than or equal to 20; and

iii) when fabricated into a film of 6 microns (micrometers) (6×10^{-6} m) has a bubble stability of at least about 260 ft/min (1.32 m/s) line speed.

16. The film of Claim 15 wherein the dart impact strength is greater than about 400 g, the film appearance rating is greater than or equal to 30 and the bubble stability is at least about 250 ft/min (1.27 m/s), the film comprising a multimodal polyethylene composition having;

1) a density of at least about 0.940 g/cm^3 as measured by ASTM D-1505;

2) a melt flow index (I_5) of from about 0.2 to about 1.5 g/10 min (as measured by ASTM D-1238, measured at 190 °C and 5 kilograms);

3) a melt flow index ratio (I_{21}/I_5) of from about 20 to about 50; and

4) a molecular weight distribution, M_w/M_n , of from about 20 to about 40;

the composition comprising;

A) a high molecular weight fraction which;

a) is present in an amount of from about 30 to about 70 weight percent (based on the total weight of the composition);

b) has a density of at least about 0.860 g/cm^3 as measured by ASTM D-1505;

c) has a melt flow index (I_{21}) of from about 0.01 to about 50 g/10 min (as measured by ASTM D-1238, measured at 190 °C and 21.6 kilograms); and

d) a melt flow index ratio (I_{21}/I_5) of from about 6 to about 15; and

B) a low molecular weight fraction which;

a) is present in an amount of from about 30 to about 70 weight percent (based on the total weight of the composition);

b) has a density of at least about 0.900 g/cm^3 as measured by ASTM D-1505;

c) has a melt flow index (I_2) of from about 0.5 to about 3000 g/10 min (as measured by ASTM D-1238, measured at 190 °C and 2.16 kilograms); and

d) a melt flow index ratio (I_{21}/I_5) of from about 5 to about 15.

17. The film of Claim 16 wherein the dart impact strength is greater than about 420 g, the film appearance rating of greater than or equal to 30 and the bubble stability is at least about 250 ft/min (1.27 m/s), and wherein for the multimodal polyethylene composition;

- 1) the density is from about 0.945 to about 0.955 g/cm³;
- 2) the melt flow index (I_5) is of from about 0.25 to about 1.0 g/10 min;
- 3) the melt flow index ratio (I_{21}/I_5) is of from about 24 to about 40; and
- 4) the molecular weight distribution, Mw/Mn is from about 22 to about 38;

the composition comprising;

A) a high molecular weight fraction which;

- a) is present in an amount of from about 40 to about 60 weight percent (based on the total weight of the composition);
- b) has a density of from about 0.890 to about 0.940 g/cm³;
- c) has a melt flow index (I_{21}) of from about 0.2 to about 12 g/10 min;
- and
- d) a melt flow index ratio (I_{21}/I_5) of from about 7 to about 12; and

B) a low molecular weight fraction which;

- a) is present in an amount of from about 40 to about 60 weight percent (based on the total weight of the composition);
- b) has a density of from about 0.910 to about 0.975 g/cm³;
- c) has a melt flow index (I_2) of from about 1.0 to about 1,000 g/10 min;
- and
- d) a melt flow index ratio (I_{21}/I_5) of from about 6 to about 12.

18. The film of Claim 17 having a dart impact strength of greater than about 400 g, a film appearance rating of greater than or equal to 40, and a bubble stability of at least about 260 ft/min (1.32 m/s).

19. The multimodal polyethylene composition of any of Claims 5, 6, 7, 10 or 11 having a NCLS of at least 2400 hours, a ratio of flexural modulus to density of at least 1140 kPa • m³/kg or both.

20. A multimodal polyethylene composition having a NCLS of at least 2400 hours, a ratio of flexural modulus to density of at least 1140 kPa • m³/kg, and an I_{21}/I_2 of at least 90.

21. A multimodal polyethylene composition having a NCLS of at least 2400 hours, and a ratio of flexural modulus to density of at least $1140 \text{ kPa} \cdot \text{m}^3/\text{kg}$ produced by a process comprising:

1) contacting in a first gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about 70°C to about 110°C , a supported titanium magnesium catalyst precursor, cocatalyst, and a gaseous composition, the gaseous composition having;

i) a mole ratio of alpha-olefin to ethylene of from about 0.01:1 to about 0.8:1; and optionally

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.001:1 to about 0.3:1,

to produce a high molecular weight polymer (HMW); and

2) transferring the HMW polymer from step 1 to a second gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about 70°C to about 110°C , with a gaseous composition having;

i) a mole ratio of alpha-olefin to ethylene of from about 0:0005:1 to about 0.01:1; and

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.01:1 to about 3:1

to form a polymer blend product; and

3) melting the polymer blend product in an extruder having a mixer vent wherein;

ii) the mixture vent has an oxygen concentration of from about 0.05 to about 6 volume percent oxygen in nitrogen; and

ii) the extrusion temperature is sufficient to melt the polymer and result in tailoring in the presence of the oxygen; and

4) passing the molten polymer blend through one or more active screens, wherein in the case of two or more active screens, the screens are positioned in series, each active screen having a micron retention size of from about 2 to about 70, at a mass flux of about 5 to about 100 lb/hr/in^2 (1.0 to 20 kg/s/m^2) to form a screened molten polymer blend.

22. A fabricated article made of the multimodal polyethylene composition of any of Claims 19, 20 or 21.

23. The fabricated article of Claim 22 which is a fiber, a wire or cable jacket, a conduit, a tape, a sheet, a pipe, a blow molded object, an injection molded object, a vacuum molded object, a rotomolded object, a thermoformed object or a combination thereof.
24. The fabricated article of Claim 23 which is a single layer or multilayer corrugated pipe.
- 5 25. The fabricated article of Claim 22 which is a multilayer structure having at least one layer having corrugation or other strength enhancing shape and at least one smooth layer.